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280–288 December

4**Organo-bentonite for the adsorption of Pb(II) from aqueous solution: Temperature dependent parameters of several adsorption equations Elroy Nathaniel, Alfin Kurniawan, Felycia Edi Soeteredjo, Suryadi Ismadji**

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1**ABSTRACT The preparation of organo-bentonite** was conducted **using**

bentonite from Pacitan as the raw material. The modification of bentonite was conducted by microwave irradiation. The adsorption capability of natural and modified-bentonite was tested for the removal of lead metal from aqueous solution. The adsorption

4**experiments were** conducted **isothermally in static mode at** various **temperatures.**

5**The temperature dependent forms of** the **Langmuir, Freundlich, Sips and Toth** models **were** used **to correlate** equilibrium **data.**

It was found that the

5**temperature dependent forms of Sips model**

can correlate the experimental data better than other models. The

25**pseudo-first-order and pseudo-second-order models were** chosen **to** correlate **the experimental** kinetic **data. The pseudo-** second **order** correlated **the**

experimental data fairly well. Keywords: Adsorption; Bentonite; Organo-bentonite; Isotherm; Temperature dependent 1. Introduction The

32**presence of heavy metals in air, soil and water** are **known to be harmful to** living **species.** The presence **of**

these substances in water such as Cr, Pb, Cd, Zn, Ni, As, Cu and Hg can affect human health because they are non-biodegradable, toxic and carcinogenic even at low concentration [1]. Among the heavy metals, lead is one of the most toxic metals due to its severe effects in human health. The presence of this metal in human body can cause several disorders and diseases such as diminishing IQ, anemia, chronic headache, high blood pressure, diarrhoea, poisoning and malfunction of reproductive and other organ systems such as liver, brain, kidney and central nerve [1,2]. Many kinds of technologies

31**are available for the removal of** lead **from water** or **wastewater** such as **chemical precipitation,** Corresponding author **ion exchange,** biological treatment,

electrochemical treatment, membrane filtration, **and**

adsorption [3]. The main advantages of using adsorption process for sequestering of lead and other heavy metals is the efficiency, selectivity, simplicity in design, and low operational cost. This process can also remove heavy metals ions even at very low concentration. However, the main drawback of this technique is the high cost of commercially available adsorbents such as activated carbon, especially for industrial wastewater treatment purpose. Accordingly, alternative low-cost and abun- dantly available materials for wastewater treatment purpose are needed. Clay has been developed as one of the potential low-cost materials in terms of

19**high specific surface area, cation exchange capacity,** chemical **and**

mechani- cal stability [4,5]. The utilization of clays for the heavy metals removal from aqueous solutions has been studied [6–16] and strongly recommended due to their E. Nathaniel

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280–288 abundant and natural availability, technical feasibility, engineering applications and cost effectiveness. Bentonite is one of the clay materials found in many countries in the world. It is originated from the volca- nic activities that contain montmorillonite, which is a 2:1 type aluminosilicates mineral [8]. Bentonite is com- posed of an Al-octahedral sheet and two Si-tetrahedral sheets. The tetrahedral sheet provide a substitution of Al3þ for Si4þ which gives a net negative charge on the clay surfaces. Moreover, montmorillonite has an amphoteric pH-dependent surface and high exchange capacity due to isomorphous substitution between Al3þ and Si4þ. These surfaces provide suitable adsorp- tion sites for cation species and make it as a potential alternative adsorbent for adsorption of heavy metals. ‘‘Bentonite deposit in East Java, Indonesia, is mainly found as Ca or Mg-type bentonite. This type of bentonite is generally suitable as raw material for adsorbent and bleaching earth. In East Java, bentonite reserves can be found in several areas such as Pacitan, Ponorogo, Blitar, Trenggalek, etc, with total reserves more than 500 million tons’’ [17]. Recently, several stu- dies about the utilization of bentonite clay for lead removal have been conducted [6,7,12], however, the utilization of Pacitan bentonite modified with linear alkylbenzene sulphonate (LAS) surfactant still not available in the literature. Therefore, by conducting this study, the potential application of Pacitan bento- nite and its modified form for sequestering of Pb(II) from wastewater is obtained. In most adsorption studies of heavy metals using clays, the equilibrium data were correlated with adsorption isotherm equations at single temperature. It is important that temperature dependence of adsorption isotherm equations should be presented in correlating equilibrium data at various temperatures.

8**To the best of our knowledge, there is no information available about the** use **of**

temperature dependence forms of adsorption isotherm equations for correlation of heavy metals adsorption data. In this study, the tem- perature dependence

5forms of Langmuir, Freundlich, Sips and Toth models were employed and the

physical meaning and validity of each parameter of the model also discussed.

82. Materials and methods 2.1. Materials Bentonite used in this study was obtained from Pacitan,

1East Java, Indonesia. The type of bentonite from this location is Ca-bentonite. Prior to the use, the bentonite was treated using H2O2 solution to

remove its organic impurities. The complete procedure about the purification of bentonite can be found elsewhere [18]. The cation exchange capacity (CEC) of bentonite was 57 meq/100 g of clay according to ASTM C837- 99 procedure. The elemental analysis of bentonite was conducted using flame atomic absorption spectrophot- ometer (SHIMADZU AA-6200). The results are given as follow: Al 39.12%, Si 47.89%, Fe 3.44%, Ca 0.15%, Mg 0.45%, K 0.24%, Na 0.47%, Mn 0.03% and H2O 8.21%. The surfactant used as modifying agent was LAS purchased from Sigma Aldrich. 2.2. Preparation of organo-bentonite The modification of bentonite was conducted by microwave heating irradiation method. The procedure was described as follow: 2 g of bentonite was added to 10 mL of surfactant solution with the concentration of LAS equal to the CEC of bentonite. The suspension was then irradiated for 5 min

1in a microwave oven (National NN-S327 WF) at heating power of 700 W. The

selection of the microwave heating procedure is due to the time efficiency and energy-saving [19]. The sample was then washed by deionized water at least three times until the pH of the washing solution did not change significantly. Subsequently, the organo-bentonite was dried in an oven at 105 C for 24 h, crushed and sieved through 100/120 mesh screen. 2.3. Characterizations of materials The characterizations of bentonite and organo- bentonite were conducted using X-ray diffraction (XRD) and FTIR technique. The XRD patterns of bento- nite and organo-bentonite

15was recorded on a Rigaku Miniflex Powder Diffractometer at 30 kV and 15 mA with Cu Ka radiation at a step size of 0.01

. The infra- red spectroscopy spectra of the materials was recorded using a FTIR SHIMADZU 8400S

6in order to identify the specific functional groups on the materials surface. The

FTIR analysis was carried out by using KBr disk proce- dure in the wavenumber range of 500–4000 cm 1 . 2.4. Adsorption experiments Adsorption experiments were carried out in a static mode at different

temperatures (30, 40 and 50 C). The adsorption isotherm study was conducted by adding various amounts of adsorbent (0.1–1.0 g) into a series of erlenmeyer flasks with glass stoppered containing

22**100 mL of metal solution at** initial concentrations **of** 200 **mg/L.**

The

19**pH of solution was adjusted to 5 by** adding an appropriate **amount of 0.**

1 N HCl. The solutions were then placed in a water-bath shaker (Memmert) and shaken at 100 rpm for 80 min at desired temperatures. After the process was E. Nathaniel

17**et al. / Desalination and Water Treatment 36 (2011)** 280–288 Fig. **1.** The XRD patterns **of**

natural and organo-bentonite. completed, the

29**flasks were removed from the bath and the**

mixtures

20**were centrifuged at** 3,500 **rpm for 5 min**

34**to separate the** solution **from the** adsorbent. **The** residual **concentration of** Pb **(II)** ions **in the** solution **was** ana- lyzed **by** flame **atomic absorption**

spectrophotometer at max of 283.3 nm. All adsorption experiments were performed in triplicate and the results were given as averages. The amount of Pb(II) ions adsorbed can be calculated by

26**using the following equation: qe ¼ ðC0 CeÞV** ; m **ð1Þ where C0 and Ce are the initial and equilibrium**

concen- trations of Pb(II) ions in liquid phase (mmol

14**/L), qe is the amount of** metal **adsorbed at equilibrium** condition (mmol **/g), V is the volume** of **solution (L) and m is the mass** of the **adsorbent (g).**

For kinetic study, the adsorption process was carried out by adding a fixed amount natural or organo-bentonite (0.5 g) into a series of 250 mL iodine flasks that contained

22**100 mL of metal solution at** initial concentrations **of** 200 **mg/L.**

The flasks were then shaken in a thermostatic water-bath shaker at certain temperature (30, 40 and 50 C). During the experiments, at certain of time interval (every 10 min), the metal solu- tion was taken from the flasks (10 mL using volumetric pipette), diluted with deionized water and centrifuged (3,500

20**rpm for 5 min).** The **residual concentration of** Pb **(II)** ions **in** solution **was analyzed using**

FAAS SHI- MADZU AA-6200.

27**3. Results and discussion 3.1.** Characterizations **of** materials **The XRD** analysis **was used to determine the** physi- cal characteristic **of the**

layer structure of the materials. The XRD patterns of natural and organo-bentonite are displayed in Fig. 1. In this figure, the basal spacing (d001) of natural and organo-bentonite is 13.6 Å (2y ¼ 6.4634) and 14.6 Å (2y ¼ 6.0268), respectively. The increase of basal spacing of organo-bentonite is Table 1 FTIR analysis results of natural and organo-bentonite Bentonite Organo-bentonite Functional groups (cm 1) (cm 1) O–H stretch (Al–OH or Si–OH) 3630 C–H stretch ((–CH2)n of LAS – structure) Asymmetric vibration – Symmetric vibration O–H bend (for adsorbed 1640 H2O) Si–O stretch (in-plane for Si- 1052 tetrahedral layer) Al–Al–OH bend 914 Si–O bend (quartz) 792 Si–O–Al bend 521 Si–O–Si bend 466 3632 2945 2861 1644 1054 918 794 526 469 due to the intercalation of LAS molecule on the interlayer spacing of bentonite, causing an expansion of its interlamellar spacing. The FTIR analysis results of natural and organo- bentonite are shown in Table 1. In this table, it can be shown that both natural and organo-bentonite had essentially the same surface groups, which are the char- acteristics of montmorillonite clay such as O–H stretch for Si–OH or Al–OH at around 3,600 cm 1; Si–O stretch (in-plane) for Si-tetrahedral layer at around 1,050

21**cm 1 ; Al–Al–OH** bend **at** around 910 **cm 1;** Si **–O** bend for quartz **at**

around 790 cm 1; Al–O–Si bend at around 520

21**cm 1 and Si–O–Si** bend **at** around 460 **cm 1.**

After modification process with LAS surfactant, the existence of new absorption peaks at around 2,940 and 2,860 cm 1 was noticed, these peaks attributed to the asymmetric and symmetric vibration of C–H stretch of methylene groups (–CH2)n in aliphatic carbon chain, respectively.

13**3.2. Effect of temperature The effect of temperature** in **the adsorption process was studied by varying the temperature** of the process **(30, 40 and 50** C). **The**

experimental results (Figs. 2 and 3) indicate that the adsorption capacity of both adsorbents increases as the temperature increases, which are the characteristic of the chemisorption and endothermic process. This may be a result of the increase of the solute mobility in solution which enhanced the

24**diffusion rate of adsorbate molecules** onto **the** adsorbent **pores. As**

the temperature increases, the viscosity of solution reduce hence dimin- ishing the liquid phase mass-transfer resistance and facilitating solute penetration. Furthermore, bentonite E. Nathaniel

3**et al. / Desalination and Water Treatment 36 (2011)** 280–288 Fig. **2.** Adsorption equilirbium data **of**

Pb(II) onto natural bentonite and the model fit of

6**(a) Langmuir, (b) Freundlich, (c) Sips and (d) Toth.**

and organo-bentonite, which belong to montmorillonite clay has a lattice with thermal expansion coefficient so that any temperature increases in the system will promote the sorption capacity [18,20]. 3.3.

30**Adsorption isotherms The adsorption equilibrium** data **of** Pb(II) **ions** onto natural **and**

organo-bentonite were correlated using several isotherm models (Langmuir, Freundlich, Sips and Toth) along with their temperature dependence forms. The Langmuir equation is a well-known iso- therm model describing the monolayer adsorption on the homogeneous surface. In this model, the adsorbate can only occupy one site. The mathematical expression of Langmuir model is given as follow: qe ¼ qm 1 þ KLCe KLCe ; ð2Þ where qe is the amount of solute adsorbed onto the adsorbent at equilibrium condition (mmol/g). The equilibrium concentration is symbolized by Ce (mmol/ L) while qm denotes the

1**maximum adsorption capacity** of **the adsorbent,** related **to the monolayer coverage** at solid surface **(mmol/g).**

The KL parameter is called as the adsorption affinity or Langmuir equilibrium con- stant (L/mmol). The temperature dependence forms of

1**Langmuir model can be expressed as follows**

[21,22]: qm ¼ q0 expðdðT T0ÞÞ; ð3Þ KL ¼ KL0 exp Q : ð4Þ RT Here q0 is the adsorption capacity (mmol/g) of adsorbent at a reference temperature T0 (taken as 298.15 K). The constant parameter relates to the expan- sion coefficient of the adsorbate is symbolized by d. The adsorption affinity at reference temperature T0 is E. Nathaniel

3**et al. / Desalination and Water Treatment 36 (2011)** 280–288 Fig. **3.**

Adsorption equilibrium data of Pb(II) onto organo-bentonite and the model fit of

6**(a) Langmuir, (b) Freundlich, (c) Sips and (d) Toth.**

symbolized by KL0,

23**R is the gas constant (8.314 J/ mol.K)** and **Q is the heat of adsorption** (kJ **/mol).** The Freundlich equation **is**

also one of the most popular two-parameter isotherm models

29**describing the adsorption** behaviour **in heterogeneous systems. The** mathematical expression **of**

Freundlich model is given as follows: qm ¼ KFC1e=n f; ð5Þ where 1/nf and KF are Freundlich parameter character- izing the heterogeneity factor and adsorption intensity [(mmol/g) (mmol/L)1/n], also called as adsorption capacity when the value of nf approaches infinite [23]. The temperature dependence forms of Freundlich model can be expressed below [21]: 1 ¼ RT nf A0 ; ð6Þ KF ¼ KF0 exp A0 aRT ; ð7Þ Here KF0 is the adsorption capacity at reference tem- perature T0 [(mmol/g) (mmol/L)1/n], a is a constant parameter and A0 is the characteristic of adsorption potential (kJ/mol). The Sips equation, which also known as Langmuir-Freundlich equation is a three-parameter models describing the adsorption phenomena in het- erogeneous system. The Sips model has the following form [21]: 1 qe ¼ qm ðKSCeÞ =ns 1 þ ðKSCeÞ 1=ns : ð8Þ The temperature dependence forms of Sips model are expressed as follow: KS ¼ KS0 exp Q T0 T 1 ; ð9Þ RT0 ns ¼ 1 n0 þ Z 1 1 T0 : ð10Þ T The temperature dependence form of adsorption capacity parameter (qm) is expressed in Eq. (3). The parameter KS0 is the adsorption affinity at T0 (L/mmol), n0 is the value of nS at T0 and Z is a constant parameter. The Toth equation, which is generally used for describing adsorption system in heterogeneous system with sub-monolayer coverage, has the following form [21]: E. Nathaniel

17**et al. / Desalination and Water Treatment 36 (2011)** 280–288 **Table 2 The**

fitted temperature dependent parameters of several isotherm models Natural Isotherm Parameters bentonite Organo-bentonite Langmuir q0 (mmol/g) 0.047 0.193 KL0 (L/mmol) 1.23 10 4 1.45 10 5 Q (Kj/mol) 27.71 33.49 (1/K) 0.0017 0.0189 Freundlich KF0 0.0034 0.0081 a/A0 1.065 1.295 A0 0.318 0.413 Sips Q0 (mmol/g) 0.047 0.204 KS0 (L/mmol) 8.574 9.528 Q (kJ/mol) 13.57 19.37 (1/K) 0.0096 0.0011 nS0 1.044 1.117 H 4.868 5.720 Toth q0 (mmol/g) 0.049 0.207 KT0 (L/mmol) 8.66 11.39 Q (kJ/mol) 29.14 38.92 (1/K) 0.0079 0.0082 nT0 0.874 0.773 H 8.453 10.771 qe ¼ qm Ce KT ð1 þ ðKT CeÞnTÞ1=nT : ð11Þ Here KT and nT are Toth parameters which are specific for adsorbate–adsorbent pairs. The heterogeneity factor is given by parameter 1/nT and if the value of this parameter is unity, Eq. (11) reduces to Langmuir equation. At very low concentrations, Toth equation also reduces to Henry's law. The mathematical expres- sion of Toth temperature dependence parameters are given below: KT ¼ KT0 exp Q RT0 nT ¼ nT0 þ Z 1 T0 T 1 ; ð12Þ T0 T ; ð13Þ where KT0 is the adsorption affinity at T0, nT0 is the parameter nT at T0 and Z is a constant parameter. The temperature dependence parameters of the Langmuir, Freundlich, Sips and Toth model were obtained by non-linear least square fit method. The following error function

4**was used as objective function to be minimized:**

SSE ¼ P qeðexpÞ qeðcalÞ 2!1=2 N ð14Þ Here qe(exp) is the actual amount of Pb(II) ions adsorbed, qe(cal) is the calculated amount of Pb(II) adsorbed and N is the number of experimental data. The adsorption equilibrium data of Pb(II) and the fitting of models are depicted in Figs. 2 and 3. The calculated temperature dependence parameters of the Langmuir, Freundlich, Sips and Toth models are listed in Table 2. It is obvious that Freundlich model fails to represent the equilibrium data of Pb(II) onto natural and organo-bentonite (Figs. 2 and 3). Other models seem can still

10**correlate the experimental data fairly well.** However, **the** judgement **of**

the validity of the model to represent the experimental data should not based on the graphical representation only and R2 value but the most important thing should based on the physical meaning of the parameters. Subsequently, we discuss the physical meaning of each isotherm para- meter in Langmuir, Sips and Toth model. We excluded the Freundlich model in further discussion since this equation failed to represent the experimental data. First, we begin our examination in the adsorption capacity parameter (q0) at T0 (298.15 K). The values of parameter q0 in Langmuir, Sips and Toth are reason- able and comparable to the values reported by other studies [10–12,16,24,25]. Based on the experimental data, it is obvious that organo-bentonite had higher adsorption capacity than the natural one. At an acid pH (5.0), the silanol groups of bentonite were proto- nated due the presence of excess Hþ ions in the solution: Si OH þ Hþ ! Si OHþ2 The electrostatic repulsion force between proto- nated silanol groups with Pb(II) ions occurred and it retarded the sorption process. The sorption process of Pb(II) occurred due to the physical interaction such as Van der Waals between the surface of bentonite and Pb(II) ions. In organo-bentonite, the presence of linear alkyl benzene sulfonate ions in the bentonite interlayer caused the formation of negative charge in the adsor- bent surface. Accordingly, electrostatic interactions between the negatively charged organo-bentonite and Pb(II) cations was taken place which enhanced the sorption capacity. The values of parameter q0 in the Langmuir, Sips and Toth model are consistent with these adsorption phenomena. The adsorbate–adsorbent interaction strength in adsorption can be represented by affinity parameter. When the value of this parameter is high, the surface E. Nathaniel

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280–288 is covered with more solute molecules as a result of stronger affinity towards the solid surface. Since the adsorption mechanism of Pb(II) ions onto organo- bentonite also involved electrostatic interaction hence the adsorbate molecules has stronger affinity towards the solid surface. The fitting results of adsorption affinity parameter of Toth (KT0) and Sips (KS0) model are consistent with experimental data. However, the KL0 parameter in the Langmuir model gives contrary results, the affinity of Pb(II) ions toward natural bentonite surface is higher than modified-bentonite. Additionally, the value of KL0 of both natural and organo-bentonite are considerably low compared with other values in most adsorption systems. Accordingly, in the subsequent discussion, we only discuss the validity of the temperature dependence form of Sips and Toth model. The

2**heat of adsorption** provides important **insights** in **the mechanism of adsorption. It is also a** crucial **thermodynamic** properties **for the design of adsorption**

system

2**to estimate the heat released (or consumed) during adsorption or desorption process.** The **values of the heat of adsorption** (Q) **can be determined either** by varying **the** temperatures during **adsorption** pro- cess **or by direct calorimetric measurements** [26]. **The**

parameter Q in Sips and Toth model

6**is only the measure of the adsorption heat**

[21]. As mentioned in previous paragraph, electrostatic interactions also occurred during the adsorption of Pb(II) ions onto organo-bentonite thus higher value of the adsorption heat is expected. The fitting results of Q parameter in Sips and Toth model is in agreement, in which the heat of adsorption of Pb(II) onto organo-bentonite is higher than natural one. The temperature coefficient of the expansion of adsorbate is represented by d, in which this parameter essentially independent of the type of adsorbent and the value is usually in the order of 10 3 K 1. The results in Table 2 show that the fitting value of d parameter in Toth and Sips model is consistent with the d values of many solutes [22]. The last examination was carried out in the parameter characterizing the system heterogeneity. This parameter is symbolized by nT0 in Toth and nS0 in Sips model. The value of this parameter

9**is usually greater than unity,** the **larger value** of n indicates **the** more heterogeneous **is**

the system. The presence of LAS molecules in the bentonite interlayer caused the adsorbent more heteroge- neous thus higher value of n is expected in the adsorption system using organo-bentonite. In Table 2, it can be seen that the fitting values of nS0 parameter in Sips model is consistent while Toth model fails to give the correct value of nT0 parameter. Based on the analysis of the physical meaning of each isotherm parameters above, it is obvious that the adsorption equilibrium data of Pb(II) fitted best with the Sips model. 3.4. Adsorption kinetics The kinetics data provide fundamental and complete description of the transport mechanisms of adsorbate into adsorbent.

9**In order to achieve the proper design of** the sorption system, **the adsorption** equilibrium data **need to be** supported **with adsorption kinetics. Several kinetic models**

are available, among them the pseudo-first-order and pseudo-second-order model are widely used to correlate experimental data [27]. Since the natural bentonite had lower adsorption capacity than the modified one, in this section, the kinetic study was only conducted for organo-bentonite. The

11**earliest known equation to describe the** sorption **rate in the liquid phase was proposed by Lagergren**

[28] and known as Lagergren

24**pseudo-first- order equation. The** expression **of** this equation **in** terms of **pseudo-** first **order**

was employed by Sharma Fig. 4. The kinetic

33**plots of (a) pseudo-first order and (b) pseudo-second order** model **for the** adsorption **of** Pb(II) **onto**

organo-bentonite. E. Nathaniel

3**et al. / Desalination and Water Treatment 36 (2011)** 280–288 **Table 3**

The fitted

30**kinetic parameters for the adsorption of** Pb(II) **onto** organo **-bentonite**

18**Pseudo-first order Pseudo-second order** T (K) **qe,** exp qe **,cal (mmol/g)** k' **(min 1) R2 qe,cal (mmol/g)** ks **(g/mmol min) R2**

313.15 0.2421 323.15 0.2532 333.15 0.2642 0.1801 0.0357 0.2091 0.0310 0.2238 0.0316 0.9716 0.2402 0.9599 0.2706 0.9568 0.2824 0.1097 0.9972 0.1153 0.9971 0.1293 0.9985

11**et al.** [29] **to correlate the sorption kinetic** data **of Ni(II)** ions into **wollastonite.**

The Lagergren pseudo-first order has mathematic expression as follows: qe qeexpð k0tÞ ¼ qt; ð15Þ where qe and qt

28**are the** amount **of** Pb **(II) ions adsorbed at equilibrium** condition **and at time t (min), respec- tively.** The **k'**

7**(min 1)** parameter **is the rate constant** for **pseudo-first order. The pseudo-second-order model is** commonly **associated with the situation when the rate of direct** adsorption **/desorption process controls the overall** sorption **kinetics**

[30]. The first mathematical expres- sion of the pseudo-second-order model was proposed by Blanchard et al. [31], which has the form as follows: qt ¼ ksq2et=ð1 þ ksqetÞ; ð16Þ where ks (g mmol 1 min 1) is the rate constant for pseudo-second-order model. The kinetic data and the model fitted are given in Fig. 4. The fitted parameters of the kinetic models are summarized in Table 3. By comparing the fitting results of pseudo-first and pseudo-second-order para- meter, both of them seem to give well correlation. However, the calculated values of qe from pseudo- first order deviate quite large from experimental data while pseudo-second order gave reasonable values. The potential advantages of the pseudo-second-order model as an expression to estimate the qe value

16**is its small sensitivity for the influence of the random** experi- mental **error.** Moreover, **the**

qe value can also be deter- mined from the

16**plot independently of the kinetic mechanism which** controls **the** sorption **process**

[30,32]. 4. Conclusions Organo-bentonite synthesized from Pacitan bento- nite using LAS as modifying agent has potential appli- cation for Pb(II) ions removal. The characterizations of materials were conducted

using FTIR and XRD techni- ques. The temperature dependent form of several adsorption isotherm equations

> 5**(Langmuir, Freundlich, Sips and Toth)** was **employed to correlate the** equili- brium **data.**

The Sips model gave best representation to the experimental data with reasonable fitted para- meters results. The kinetic data for the adsorption of Pb(II) ions onto organo-bentonite was best represented by the pseudo-second order model. References [1] D. Sud, G. Mahajan and M.P. Kaur, Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions – A review, Bioresour. Technol., 99 (2008) 6017–6027. [2] L. Wang, J. Zhang, R. Zhao, Y. Li, C. Li and C. Zhang, Adsorp- tion of Pb(II) on activated carbon prepared from Plygonium orientale Linn.: Kinetics, Isotherms, pH, and ionic strength stu- dies, Bioresour. Technol., 110 (2010) 5808–5814. [3] F. Fu and Q. Wang, Removal of heavy metal ions from waste- waters: A review, J. Environ. Manage., 92 (2011) 407–418. [4] D.S. Tong, C.H. Zhou, Y. Lu, H. Yu, G.F. Zhang and W.H. Yu, Adsorption of acid red G dye on octadecyl trimethylammonium montmorillonite, Appl. Clay Sci., 50 (2010) 427–431. [5] D. Zhang, C.H. Zhou, C.X. Lin, D.S. Tong and W.H. Yu, Synth- esis of clay minerals, Appl. Clay Sci., 50 (2010) 1–11. [6] A.R. Kul and H. Koyuncu, Adsorption of Pb(II) ions from aqu- eous solution by native and activated bentonite: Kinetic, equili- brium, and thermodynamic study, J. Hazard. Mater., 179 (2010) 332–339. [7] S. Wang, Y. Dong, M. He, L. Chen and X. Yu, Characterization of GMZ bentonite and its application in the adsorption of Pb(II) from aqueous solutions, Appl. Clay Sci., 43 (2008) 164–171. [8] T.S. Anirudhan and P.S. Suchithra, Equilibrium, kinetic, and thermodynamic modeling for the adsorption of heavy metals onto chemically modified hydrotalcite, Indian J. Chem. Tech- nol., 17 (2010) 247–259. [9] M. Eloussaief and M. Benzina, Efficiency of natural and acid activated clays in the removal of Pb(II) from aqueous solutions, J. Hazard. Mater., 178 (2010) 753–757. [10] E. Eren, Removal of lead ions by Unye (Turkey) bentonite in iron and magnesium oxide-coated forms, J. Hazard. Mater., 165 (2010) 63–70. [11] M. Hamidpour, M. Afyuni, M. Kalbasi, A.H. Khoshgoftarmanes and V.J. Inglezakis, Mobility and plant-availibility of Cd(II) and Pb(II) adsorbed on zeolite and bentonite, Appl. Clay Sci., 48 (2010) 342–348. [12] J.A. Hefne, W.K. Mekhemer, N.M. Alandis, O.A. Aldayel and T. Alajyan, Kinetic and thermodynamic study of the adsorption of Pb(II) from aqueous solution to the natural and treated bento- nite, Int. J. Phys. Sci., 3 (2008) 281–288. [13] Bna.Im.Oiclsuo-Oftwhoelraebmioavnadl oEf.IZ.nU2nþuaanbdonCauh2,þKfrinoemticaqaunedouthsesromluotdioyn- by sulphate and phosphate-modified Bentonite clay, J. Hazard. Mater., 184 (2010) 731–738. E. Nathaniel et al. / Desalination and Water Treatment 36 (2011) 280–288 [14] J.U.K. Oubagaranadin and Z.V.P Murthy, Isotherm modeling and batch adsorber design for the adsorption of Cu(II) on a clay containing montmorillonite, Appl. Clay Sci., 50 (2010) 409–413. [15] M. Sprynsky, B. Buszewski, A.P. Terzyk and J. Namiesnik, Study of selection mechanism of heavy metal (Pb2þ, Cu2þ, Ni2þ and Cd2þ) adsorption on clinoptilolite, J. Colloid Interface Sci., 304 (2006) 21–28. [16] M.G.A. Vieira, A.F.A. Neto, M.L. Gimenes and M.G.C. Silva, Sorption Kinetic and equilibrium for the removal of nickel ions from aqueous phase on calcined Bofe bentonite clay, J. Hazard. Mater., 177 (2009) 362–371. [17] R. Koswojo, R.P. Utomo, Y.H. Ju, A. Ayucitra, F.E. Soetaredjo, J. Sunarso and S. Ismadji, Acid green 25 removal from wastewater by organo-bentonite from Pacitan, Appl. Clay Sci., 48 (2010) 81–86. [18] A. Kurniawan, H. Sutiono, Y.H. Ju, F.E. Soetaredjo, A. Ayucitra, A. Yudha and S. Ismadji, Utilization of rarasaponin natural sur- factant for organo-bentonite preparation: Application for methylene blue removal from aqueous effluent, Micropor. Mesopor. Mater., 142 (2011) 184–193. [19] C.H. Zhou, Emerging trends and challenges in synthetic clay- based materials and layered double hydroxides, Appl. Clay Sci., 48 (2010) 1–4. [20] A.S. Ozcan, B. Erdem and A. Ozcan, Adsorption of acid blue 193 from

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